Macromol. Symp. **2003**, *203,* 147-154

Depth Profiling of Polymer Films by Confocal Raman Spectroscopy

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Summary: Confocal Raman microspectroscopy has many potential applications in the study of polymer-solvent interactions, including the determination of solvent and polymer-solvent complex depth profiles. This contribution focuses on preventing the formation of polymer-solvent complexes, using surface chemical modification of PVC films. While the surface-specific nature of the film modification is easily demonstrated,[1] confocal Raman measurements clearly show the effects of film refractive index: the modifier depth profile shows a lack of symmetry and the film thickness is underestimated. A spectral normalisation method is described, and this is shown to result in a modifier depth profile which is in good agreement with data obtained by Raman microspectroscopy following physical cross-sectioning of a sample. Alternative techniques for Raman depth profiling are also discussed.

Keywords: confocal Raman spectroscopy; depth profile; polymer; PVC films

Introduction

The technique of confocal Raman microspectroscopy has considerable potential for the rapid, non-destructive analysis of inhomogeneous polymer films. In the context of polymer-solvent interactions, there are several fruitful areas of application, including depth profiling of a polymer film which has been exposed to solvent. In this case, the extent of formation of a polymer-solvent complex may be studied, or the progress of solvent into the film. For a glassy polymer film, the progression of a solvent/swollen glass front through the film may be monitored as a function of time. Our interest has been in the characterisation of polymer films whose surfaces have been chemically modified to prevent formation of polymer-solvent complexes.

The controlled chemical modification of polymer films was a major objective of this work, using

DOI: 10.1002/masy.200351313

a solvent/non-solvent mixture as the reaction medium. Here we use the example of PVC modified with aminothiophenol. Film preparation is described in detail elsewhere.[1,2] PVC films of thicknessness 10-100 μm were modified in this way.

Confocal Raman Microspectroscopy

A Renishaw Ramascope 2000 spectrometer was used, with excitation from the 632.8 nm line of a He-Ne laser. Further details are provided elsewhere.[3] A spectral resolution of approximately 3 cm^{-1} was used.

The confocal Raman technique has the advantages of being rapid and non-destructive. In addition, the depth of sample accessible, typically up to 100 μm, is significantly greater than that available from other depth profiling techniques, such as XPS or ATR. The limiting depth resolution in air, often determined using a silicon wafer, is in the region of 2 μm. However, this figure is substantially modified by the refractive index of the polymer film, as will be demonstrated here.

A Raman band characteristic of the modifier species is required for depth profiling. In this case, the 1596 cm^{-1} aromatic stretching vibration was used, with the 1425 cm^{-1} C-H stretching vibration of unmodified PVC used for spectral normalization.

Depth Resolution

The question of sample refractive index has recently been raised, in relation to depth resolution obtainable from confocal Raman microspectroscopy. Everall[4,5] has used a simple ray-tracing analysis to investigate the effect of refractive index on both the focal point and the depth of focus of the microscope objective. The apparent focal distance, Δ, of a ray originating from a distance z_m below the air/polymer interface was found to be related to z_m through:

$$z_m = \Delta\left(m^2 \frac{(NA)^2(n^2-1)}{(1-NA^2)} + n^2 \right)^{1/2} \qquad (1)$$

where the normalised radius, m, of a ray incident on the objective lens is r_k/r , r and NA are the radius and numerical aperture of the objective and n is the refractive index of the polymer film.

Furthermore, the depth of focus was found to increase with depth as:

$$\text{Depth of Focus} = z_m - \Delta n \qquad (2)$$

Equations (1) and (2) have serious impications for the use of the confocal Raman technique in depth profiling. It was shown[4] that, for a Gaussian radial intensity distribution of the laser beam incident on the objective lens, at an apparent film depth (Δ) of only 10 μm, the film is sampled to depths greater than 25 μm. This immediately calls into question the use of this technique to study features such as the positions and extent of any interfaces present.

The purpose of this work is to investigate possible effects of sample refractive index on our Raman data and to compare depth profiles obtained using normalised confocal spectra with those found by physical cross-sectioning a sample and using conventional Raman spectroscopy. Thus, we aim to evaluate the confocal technique in relation to alternative methods, such as physical cross-sectioning or the use of an oil immersion objective.

Raman Results

Two depth profiles were obtained from a PVC film modified with aminothiophenol. After the first set of measurements, the sample was inverted to obtain the second set. In both cases, the sample was in contact with air on either side, in the region of the laser beam.

Figure 1 shows the two sets of raw Raman data. In Figure 1 (a), the microscope has been moved, in steps of 1.0 μm, sufficiently to allow maxima in the modifier band intensity to be observed from both the film surfaces. In Figure 1 (b), a combination of 1.0 and 2.0 μm steps was used and the experiment was stopped short of the bottom surface. Both modifier and polymer peak intensities are plotted for both sample arrangements in Figure 2.

From Figure 2 (a), it is clear that the modifier band intensity at the top surface exceeds that at the bottom surface. This might be taken as evidence that the chemical modification has progressed further on the top surface than on the lower one. However, the corresponding profile in Figure 2 (b), after inverting the sample, appears almost identical.

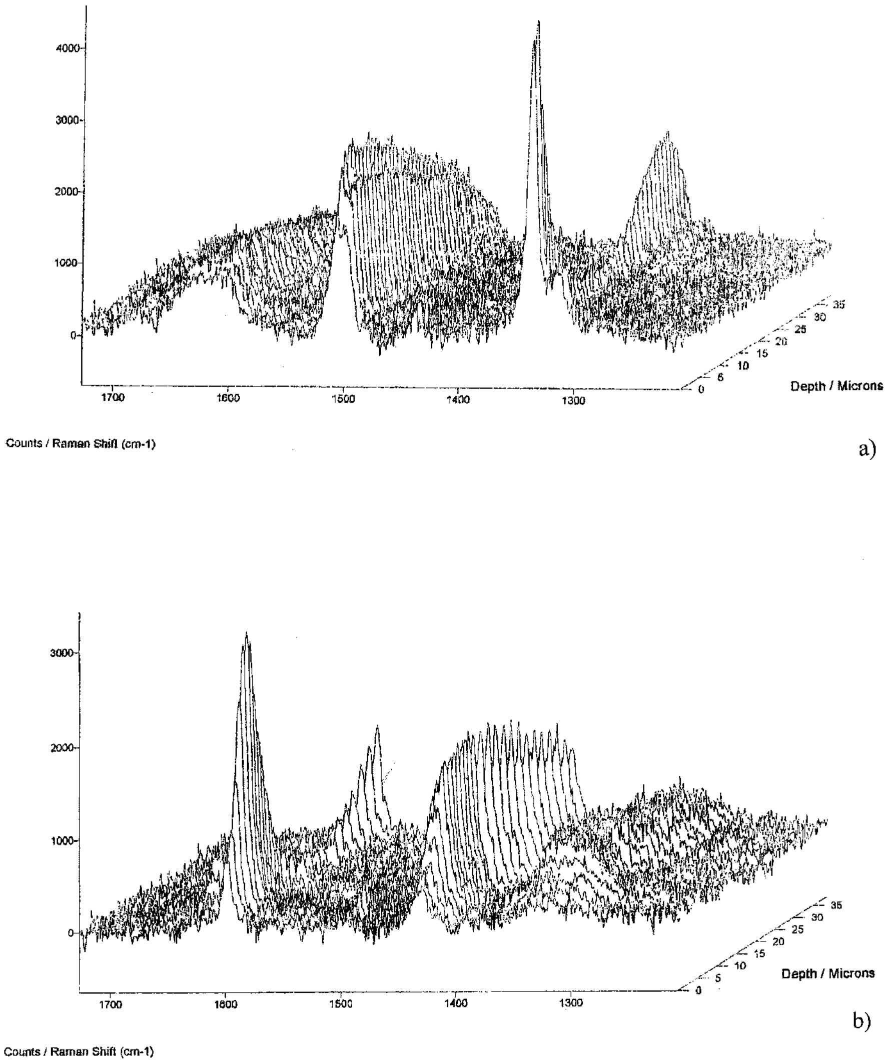

Fig. 1. Confocal Raman spectra of an 81 μm film of PVC modified with aminothiophenol. (a) shows one orientation of the film and (b) refers to the inverted film. Bands at 1596 and 1425 cm^{-1} are characteristic of modifier and polymer repectively. Axes: Vertical: intensity (counts); Horizontal: frequency (cm^{-1}); Depth: apparent depth in film (μm). Effects of refractive index are clear in the intensity variation.

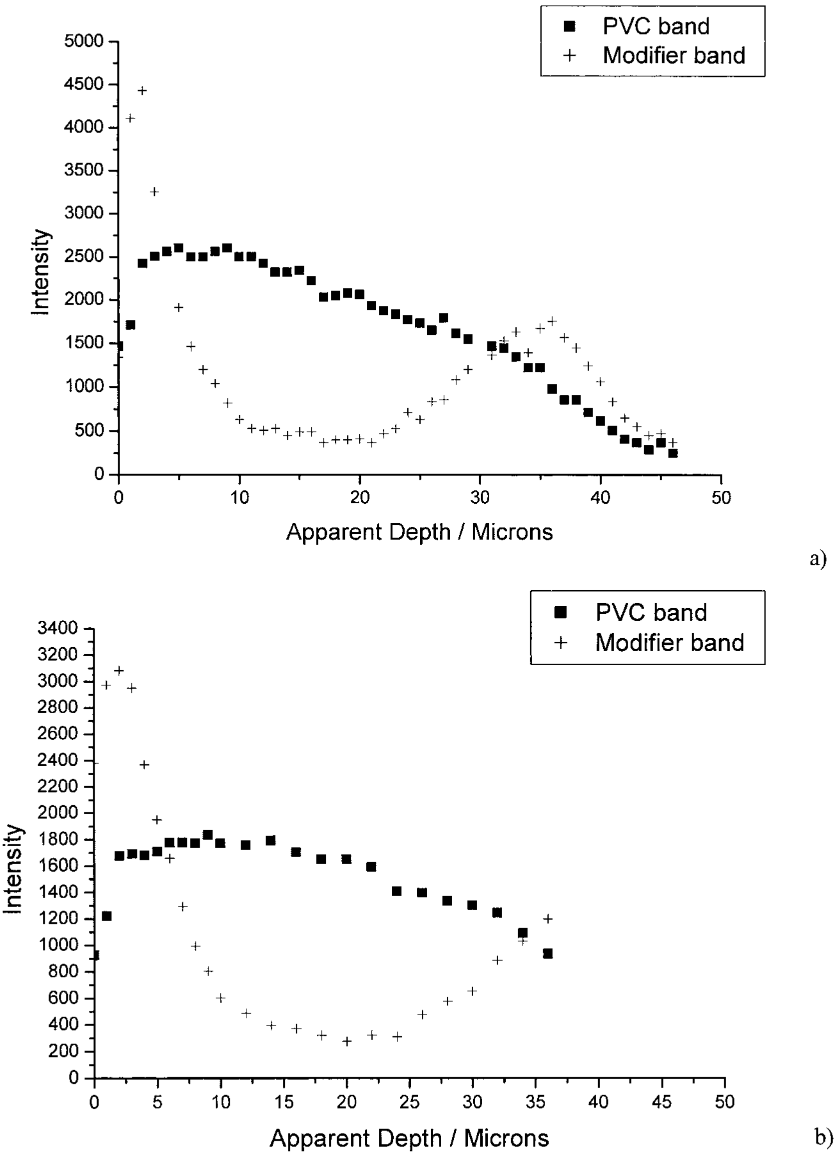

Fig. 2. Depth profiles of modifier and polymer, as determined directly from Figure 1. Results from the two sample orientations are almost identical.

The similarity of the two data sets can be attributed to the effect of sample refractive index. Furthermore, the peak in modifier intensity at the lower surface is noticeably broader than at the upper surface, indicating the deteriorating depth of focus with sample depth. In addition, the apparent film thickness, as measured from the modifier peak intensity positions, is significantly less than the value of 81 μm measured with a micrometer.

Normalisation Procedure

Having established that the polymer refractive index significantly affects the Raman spectra obtained, the data above were compared with spectra collected from a cut sample. Before making this comparison, the confocal data were normalised. The 1425 cm^{-1} PVC peak was used to normalise intensities and the thickness scale was expanded to the true value of 81 μm. The apparent film thickness was obtained by locating the two positions where the polymer Raman peak had fallen to a half of its maximum intensity, and this value was then scaled to 81 μm.

Physical Cross-Sectioning

The sample of surface-modified PVC was carefully cross-sectioned while held under liquid nitrogen. It was then mounted edge-on, between two steel blocks, for conventional Raman spectroscopy. This method makes use of the high lateral resolution (1-2 μm) available.

Figure 3 shows depth profiles obtained in this way for confocal Raman data and for conventional Raman measurements on the cross-sectioned film, in the latter case for data normalised as described above. The modifier percentage scale was obtained after calibration, using a series of bulk-modified PVC films, where the modifier concentration was determined using ^{1}H NMR spectroscopy.

As viewed in the optical microscope, the bottom surface of the cross-sectioned film showed some evidence of physical damage. This explains the lower apparent concentration for the cross-sectioned film at the lower surface (81 μm). The agreement between the two sets of data in this region is therefore probably fortuitous, while the similar lack of symmetry in the confocal data is attributable to refractive index effects. Nevertheless, there is good agreeement in the depth region from 0 to 40 μm, which validates the use of the confocal technique for these sample depths.

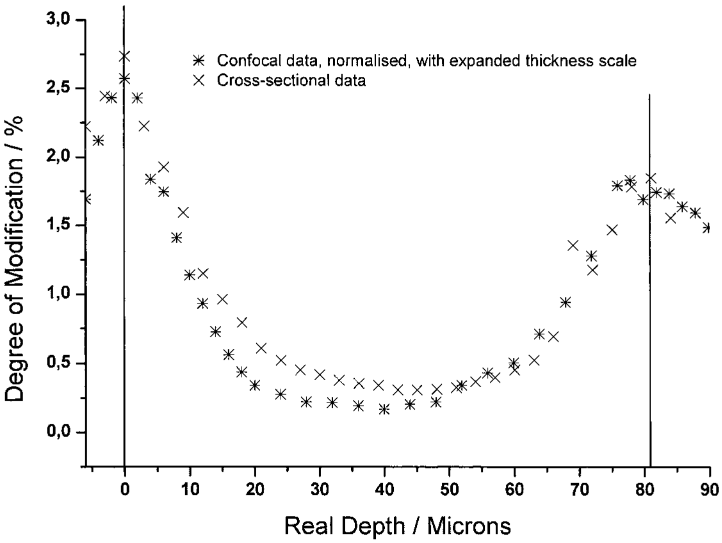

Fig. 3. A comparison between the modifer depth profile from confocal Raman measurements, after appropriate intensity normalisation and thickness scaling (*), and the depth profile from a physically cross-sectioned sample, using conventional Raman spectroscopy (X). Vertical lines indicate the film surfaces.

Conclusions

Confocal Raman microspectroscopy is seen to be a powerful technique for the rapid, non-destructive analysis of surface-modified polymer films. It has a high limiting depth resolution and high sensitivity. It is worth considering here the limitations of the technique. Locating a sharp interface, such as the solvent/swollen glass front in a polymer exposed to solvent, clearly presents some difficulties. In this case, it may be more appropriate to use an oil immersion objective or to use the iterative refinement of a model concentration profile to calculate the confocal Raman depth profile. This latter method is illustrated and discussed elsewhere.[3] The use of oil immersion objectives has the additional complications of Raman bands from the oil used and possible interaction between the oil and polymer. Measurement of the extent of an interfacial layer within a polymer film presents similar difficulties.

Nevertheless, there are areas where confocal Raman microspectroscopy is particularly useful in analysing physical or chemical variations within polymer films. Uses include the study of chemical modification, the presence of dopants of diffusants, the variation of either crystallinity or disorder and of molecular orientation. In many of these situations, physical cross-sectioning of films is either impossible or impracticable.

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